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# **The influence of additives on the fate of plastics in the marine environment, exemplified with barium sulphate**

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## **Abstract**

With an inherent density marginally below that of seawater, polyolefins (polyethylene-polypropylene) are predicted to float or undergo beaching in the marine environment. Polyolefins commonly observed on the seabed, therefore, require additional considerations that are usually based around increasing density through fouling or packaging into sinking faecal matter. Here, however, we propose that the presence of additives is of least equal significance to the behaviour of such plastics in marine systems. We compared barium, present largely as the filler, BaSO<sub>4</sub> (density = 4.5 g cm<sup>-3</sup>), in consumer and beached plastics and established that the metal was more abundant and occurred at higher concentrations in the former samples, consistent with the environmental fractionation of plastics based on additive content. Significantly, the Ba content of polyolefins required to confer a density above seawater is about 13,000 mg kg<sup>-1</sup>, a value that was exceeded in many consumer plastics but never observed in beached samples.

**Keywords:** marine plastics; additives; barium; XRF; density; fractionation

## 1. Introduction

The behaviour and (eco)toxicological effects of plastic litter in the aquatic environment, and in particular of microplastics, are generally discussed or modelled as though materials are ‘pure’ polymers (Cole et al., 2015; Chubarenko et al., 2016; Yin et al., 2018; Kaiser et al., 2019; Richard et al., 2019). A central tenet of many of these studies is that transport and fate is dictated by density, with polymers whose densities are lower than water subject to transportation at or near the surface and deposition on shorelines and polymers with densities greater than water subject to sinking and accumulation in benthic environments (Zhang, 2017; Collins and Hermes, 2019). This assumption, however, ignores the fact that most manufactured plastic products contain a variety of additives and residues whose specific densities are often well above unity (Pritchard, 1997; Papazoglou et al., 2004; Hansen et al, 2013; Shaw and Turner, 2019). A variety of functional additives that are based on simple mineral or more complex organic compounds are employed in plastics and include antimicrobials, biostabilisers, antioxidants, antistatic agents, external and internal lubricants, fillers, extenders, flame retardants, fragrances, heat and light stabilisers, impact modifiers, pigments for colour and plasticisers.

Compounds of Ba, including barium sulphide, barium carbonate, barium stearate and barium sulphate, have found widespread usage in various plastics, with BaSO<sub>4</sub> being the most commonly applied as an inert, white filler and extender, especially where an increase in specific gravity is required (Gooch, 2011). Barium compounds are among the densest used in plastics and, unlike other dense additives based on heavy metals (e.g. Pb and Cd), their presence has not been subject to restrictions based on environmental and health grounds.

Barium itself is a silvery-white Group IIA alkaline earth element that occurs in nature largely as the minerals barite ( $\text{BaSO}_4$ ) and witherite ( $\text{BaCO}_3$ ). Barium is a non-essential element for living organisms and in soluble form is very toxic, with some compounds (e.g.  $\text{BaCl}_2$ ) used as an insecticide. However,  $\text{BaSO}_4$  is so poorly soluble in water that it is considered to be non-toxic and is even used in medical applications as a contrast medium (Menzie et al., 2008; Nielsen and Ladefoged, 2013). As noted above, the presence of Ba in plastics is not regulated although its migration into a solution mimicking the human stomach (0.07 M HCl) from toys is limited to between 375 and 18,750  $\text{mg kg}^{-1}$ , depending on the physical characteristics of the material, according to the latest iteration of the European Toy Safety Directive (Turner, 2018).

In this study we report on X-ray fluorescence (XRF) measurements of Ba in both plastic consumer products and in plastics retrieved from the strandlines of beaches in order to evaluate the occurrence and concentrations of the metal across a wide range of contemporary and historical materials. Given the high density of Ba compounds (e.g.  $\text{BaSO}_4 = 4.5 \text{ g cm}^{-3}$ ), we explore the hypothesis that the amount of Ba present as an additive in low density plastics, such as polypropylene and high density and low density polyethylene (and known collectively as polyolefins), may impact on their fate in the marine environment.

## **2. Materials and methods**

### *2.1. Sample collection and categorisation*

Plastic samples for the present study had been acquired as part of independent research projects (Turner and Solman, 2016; Turner and Filella, 2017; Turner, 2018) or were collected or purchased specifically for the present study. We focused on rigid or semi-rigid plastics, avoiding rubber and foams, in both consumer products and beached litter.

Consumer plastics ( $n = 342$ ) included single use and multi-use food and cosmetic items, toys, containers and bottles, decorations, construction consumables and other plastics that enter the conventional municipal waste stream and whose age range spans 50 years. Note that we excluded electronic insulation and housings that are, in principle, disposed of separately for material recovery. Polymeric composition was noted from standard resin codes, where evident, or from previous characterisation, if undertaken. Littered plastics visible to the naked eye were collected from the strandlines of a variety of sandy beaches in south west and southern England, hereafter categorised as Atlantic (three beaches facing the Atlantic Ocean:  $n = 95$ ), urban (two beaches within the urbanised reaches of Plymouth Sound:  $n = 55$ ) and Channel (one English Channel facing beach:  $n = 43$ ). To be as consistent as possible with consumer plastics, we avoided samples that had a distinctive marine or industrial source, like fishing rope and cord and beads for waste water treatment, and focussed on primary or secondary plastics more representative of municipal waste. Distinctive items retrieved included toys, bottles and bottle tops, cartridges, nozzles, caps, cotton buds, crate strapping and piping. Offcuts of a few mg from samples collected from the Channel beach were analysed by attenuated total reflectance Fourier-transform-infrared (ATR-FTIR) spectrometry using a Bruker Vertex 70 in order to identify component polymers.

## *2.2. XRF analysis*

Samples were analysed by energy-dispersive FP-XRF using a Niton XL3t 950 He GOLDD+ that was employed either in the laboratory and in an accessory stand or in situ and handheld. The instrument was operated in a customised, standardless ‘plastics’ mode with a thickness correction algorithm employed for samples between 50  $\mu\text{m}$  and 12 mm in depth. Sample thickness was determined through the measurement surface

using Allendale digital callipers and, where possible and to reduce counting error, thickness was increased by layering or folding material.

Samples were counted for Ba and Cl (as a proxy for polyvinyl chloride, PVC, and defined as having a concentration  $> 15\%$ ) amongst a range of elements for periods ranging from 30 to 180 s, depending on thickness, that were distributed equally or in a 2:1 ratio between a low energy range (20 kV and 100  $\mu\text{A}$ ) and main energy range (50 kV and 40  $\mu\text{A}$ ). Spectra were quantified by fundamental parameter coefficients to yield concentrations on a dry weight basis (in  $\mu\text{g g}^{-1}$ ) and with a counting error of  $2\sigma$  (95% confidence). As a performance check, a 13-mm thick polyethylene reference disc (Niton PN 180-619, Lot # T-81) that had been impregnated with Ba at a concentration of  $688 \pm 45 \text{ mg kg}^{-1}$  was analysed throughout each measurement session, with the instrument returning an average concentration of  $721 \text{ mg kg}^{-1}$  ( $n = 22$ ). Precision, as the relative standard deviation arising from quintuplicate measurements of selected samples, ranged from 8 to 17%.

According to the manufacturer, the instrument detection limit for Ba in polyethylene of infinite thickness and counted for 30 s is  $100 \text{ mg kg}^{-1}$ . This value increases with decreasing thickness and decreases with increasing counting time and for our samples and operating conditions detection limits, derived from the lowest counting errors arising from each analytical batch, ranged from about 95 to  $250 \text{ mg kg}^{-1}$ . The high and variable detection limit for Ba compared with other elements results from an overlap of its  $\text{L}\beta$  line by a stronger Ti  $\text{K}\beta$  peak and a  $\text{K}\alpha$  line of low sensitivity that is located at 32.19 keV and towards the maximum energy discharged by the X-ray source (Conrey et al., 2014). It is, therefore, important to appreciate these constraints when we report concentrations of Ba that were detected.

### 3. Results

#### 3.1. Polymer composition

Most of the single use consumer items considered were constructed of polyethylene, polypropylene or polyethylene terephthalate (PET), while multi-use items, where signage was evident, displayed a broader variety of polymeric materials that included, additionally, polystyrene, acrylonitrile butadiene styrene (ABS), polycarbonate and PVC. Of the beach litter plastics analysed by FTIR ( $n = 43$ ), 17 were polyethylene, 21 were polypropylene, four were blends of (presumably recycled) polyethylene and polypropylene and one was PVC.

#### 3.2. Barium concentrations and distributions

The number of cases in which Ba was detected by XRF, along with summary statistics for concentrations (where returned), are shown in Table 1 for beached plastic litter and consumer plastics. Figure 1 presents Ba concentrations in ascending order and in terms of frequency distribution for the two sample categories. Barium was detected in more than 40% of the consumer items analysed with concentrations ranging from 243 to 105,000 mg kg<sup>-1</sup> and dominated by measurements in the 1000 to 5000 mg kg<sup>-1</sup> interval. The metal was detected in a broad range of products and polymer types of different ages of manufacture that included polyethylene- and polypropylene-based toys, polystyrene cases, and PET- and polyethylene-based single-use food packaging and food utensils. Barium was also commonly present in products constructed of PVC (as defined by the Cl content returned by the XRF), including toys and sports gear. Significantly, at least 59 samples out of 112 consumer plastics in which Ba was detected were of low density, polyethylene or polypropylene construction.



Regarding beached litter, Ba was detected by XRF in < 10% of all samples analysed and in only one sample from the Channel beach. The maximum concentration of about 11,000 mg kg<sup>-1</sup> was encountered in an item of PVC packaging from an urban beach, and the remaining Ba-positive samples were dominated by the 1000 to 5000 mg kg<sup>-1</sup> concentration interval and by bottle tops ( $n = 6$ ) and fragments of unknown origin ( $n = 8$ ) that spanned a variety of colours, including colourless. Despite an overall mean Ba concentration that was considerably lower in beached plastics (2320 mg kg<sup>-1</sup>) than in consumer plastics (6890 mg kg<sup>-1</sup>), an independent two sample  $t$ -test revealed no significant difference between the two categories ( $p = 0.09$ ).

#### **4. Discussion**

The inherent densities of polyolefin thermoplastics (polyethylene and polypropylene) are in the range 0.9 to 1.0 g cm<sup>-3</sup> and considerably lower than the densities of the remaining polymers encountered in consumer products (for instance, the densities of polycarbonate, PET and PVC are typically above 1.2 g cm<sup>-3</sup>). Thus, assuming that consumer plastics are broadly representative of plastic waste entering the environment, a natural selection of beached plastics according to density is predicted. Specifically, polyolefin densities below that of coastal seawater (about 1.02 g cm<sup>-3</sup>) ensure that this material evades sinking and is subject to long-term transportation in suspension or beaching on the strandline while denser material is deposited in the benthic environment and closer to its point of origin (Schwarz et al., 2019). This assertion is consistent with the observations in the present study and findings of other studies where beached plastics are dominated by polyolefins (Andrades et al., 2018; Brignac et al., 2019; Chen and Chen, 2020), with occasional denser objects (e.g. PVC) only washed up during certain weather conditions or when entangled with natural benthic material like kelp

that is sometimes deposited in the intertidal zone (Massos and Turner, 2017; Turner et al., 2020).

This selection of material based on inherent polymer density does not, however, account for cases in which polyolefins have been detected in sediments of the seabed over a wide range of water depths (Vianello et al., 2013; Frère et al., 2017; Cheang et al., 2018; Mu et al., 2019; Mistri et al., 2020). Some authors attribute their presence here to an increase in density and settling velocity through chemical or biological fouling or to incorporation of fragments into sinking biological aggregates like faecal material (Long et al., 2015; Cole et al., 2016; Koelmans et al., 2017). These effects become more important with decreasing particle size and increasing surface area (Ryan, 2015; Kooi et al., 2017) but may only result in temporary deposition since fouled precipitates dissolve and faecal pellets disaggregate much more quickly than the rates at which plastics degrade.

A plausible alternative, however, and one that accounts for the more permanent deposition of polyolefins of a range of size on the seafloor, is that the density of some formulations of polyethylene or polypropylene is sufficiently high to facilitate sinking through the presence of chemical additives in the matrix. Corcoran et al. (2015) suggested that the occurrence of polyethylene and polypropylene fragments in bottom sediments of Lake Ontario might result from the presence of a range of mineral fillers of moderate density, like talc and calcium carbonate ( $\rho \sim 2.7 \text{ g cm}^{-3}$ ), and other additives. An important, more general implication is that the environmental behaviour and fate of plastics constructed of polymers whose inherent densities are just below that of water could be sensitive to the precise nature and concentration of functional additives.

Results reported herein are qualitatively consistent with this assertion in that Ba-based additives are more commonly encountered and at higher (mean) concentrations in consumer plastics than in beached plastics. From a quantitative perspective, we may calculate the effects of increasing the fractional contribution of an additive,  $f_A$ , of density,  $\rho_A$ , on the density of polyethylene or polypropylene,  $\rho_P$ , from mass balance:

$$\rho_{PA} = (1 - f_A) \rho_P + f_A \rho_A \quad (1)$$

where  $\rho_{PA}$  is the net density of the amended plastic. With respect to Ba, and assuming that the metal is present as the filler, BaSO<sub>4</sub> ( $\rho_A = 4.5 \text{ g cm}^{-3}$ ):

$$\rho_{PA} = (1 - [\text{Ba}]/5.89 \times 10^5) \rho_P + [\text{Ba}] \rho_A / 5.89 \times 10^5 \quad (2)$$

where the concentration of Ba is in  $\text{mg kg}^{-1}$  and  $5.89 \times 10^5$  accounts for unit conversion and the mass contribution of the metal to the compound. Figure 2 shows the predicted change in density of a polyolefin (of median  $\rho_P = 0.94 \text{ g cm}^{-3}$ ) arising from increasing Ba concentration up to  $50,000 \text{ mg kg}^{-1}$ . Significantly, and as annotated, an added Ba concentration of  $13,200 \text{ mg kg}^{-1}$  is sufficient to raise the density to that of coastal seawater and alter the environmental fate and (photolytic) degradation rate of the plastic. This concentration was exceeded in 17 consumer plastics, of least five of which were polyolefin in construction, but was never exceeded among the beached plastics analysed. On this basis, therefore, we predict that polyolefins in the marine environment that have a Ba content in excess of a critical value of  $13,200 \text{ mg kg}^{-1}$  will accumulate on the seafloor of temperate coastal regions, with sinking in fresh water or deep ocean environments requiring slightly less than or more than this concentration, respectively. On the other hand, polyolefins containing lower concentrations of Ba are predicted to remain in suspension or become beached. Significantly, the behaviour of polyolefins

whose Ba content is close to the critical value may be particularly sensitive to additional environmental factors, such as fluctuations in salinity or temperature, the degree of biofouling and the rate of leaching of the additive from the matrix.

Of course, in reality manufactured plastics may contain a range of additives that have been deliberately added during manufacture or incorporated inadvertently through recycling that further increase density or reduce the amount of Ba required to reach a critical density equal to that of seawater. Where Ba was detected in consumer goods by XRF it was generally the main additive in terms of mass, although X-ray spectra often revealed important contributions from compounds of Fe, Ti and Zn and traces of compounds of Cu, Pb and Sb.

An additional consequence of the environmental fractionation of polyolefins according to additive content is the exposure to greater quantities of potentially harmful compounds in benthic habitats through incidental ingestion of plastic. Thus, BaSO<sub>4</sub> itself very insoluble (285 mg L<sup>-1</sup> in water at 30°C; Ropp, 2013) but plastic could be a source of microscopic filler particles whose size range (2 to 70 µm for BaSO<sub>4</sub>; Pritchard, 1997) presents a risk of being accumulated and translocated (Cole et al., 2015; Fernandez and Albentosa, 2019). Other, dense and harmful additives used historically in polyethylene and polypropylene for colour include lead chromate and cadmium sulphate (Hansen et al., 2013; Turner, 2018) and while occasionally reported in beached plastics (Turner and Solman, 2016; Massos and Turner, 2017), we surmise that higher concentrations are likely in benthic accumulations.

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## References

- Andrades, R., Santos, R.G., Joyeux, J.C., Chelazzi, D., Cincinelli, A., Giarrizzo, T., 2018. Marine debris in Trindade Island, a remote island of the South Atlantic. *Marine Pollution Bulletin* 137, 180-184.
- Brignac, K.C., Jung, M.R., King, C., Royer, S.J., Blickley, L., Lamson, M.R., Potemra, J.T., Lynch, J.M., 2019. Marine debris polymers on main Hawaiian Island beaches, sea surface and seafloor. *Environmental Science and Technology* 53, 12218-12226.
- Cheang, C.C., Ma, Y., Fok, L., 2018. Occurrence and composition of microplastics in the seabed sediments of the coral communities in proximity of a metropolitan area. *International Journal of Environmental Research and Public Health* 15, 2270, DOI: 10.3390/ijerph15102270
- Chen, M.C., Chen, T.C., 2020. Spatial and seasonal distribution of microplastics on sandy beaches along the coast of the Hengchun Peninsula, Taiwan. *Marine Pollution Bulletin* 151, 110861.
- Chubarenko, I., Bagaev, A., Zobkov, M., Esiukova, E., 2016. On some physical and dynamical properties of microplastic particles in marine environment. *Marine Pollution Bulletin* 108, 105-112.
- Cole, M., Lindeque, P., Fileman, E., Halsband, C., Galloway, T.S., 2015. The impact of polystyrene microplastics on feeding, function and fecundity in the marine copepod *Calanus helgolandicus*. *Environmental Science and Technology* 49, 1130-1137.
- Cole, M., Lindeque, P., Fileman, E., Clark, J., Lewis, C., Halsband, C., Galloway, T.S., 2016. Microplastics alter the properties and sinking rates of zooplankton faecal pellets 50, 3239-3246.
- Collins, C., Hermes, J.C., 2019. Modelling the accumulation and transport of floating marine micro-plastics around South Africa. *Marine Pollution Bulletin* 139, 46-58.
- Conrey, R.M., Goodman-Elgar, M., Bettencourt, N., Seyfarth, A., Van Hoose, A., Wolff, J.A., 2014. Calibration of a portable X-ray fluorescence spectrometer in the analysis of archaeological samples using influence coefficients.

- Corcoran, P.L., Norris, T., Ceccanese, T., Walkaz, M.J., Helm, P.A., Marvin, C.H., 2015. Hidden plastics of Lake Ontario, Canada and their potential preservation in the sediment record. *Environmental Pollution* 204, 17-25.
- Fernandez, B., Albentosa, M., 2019. Dynamic of small polyethylene microplastics ( $\leq 10 \mu\text{m}$ ) in mussel's tissues. *Marine Pollution Bulletin* 146, 493-501.
- Frère, L., Paul-Pont, I., Rinnert, E., Petton, S., Jaffré, J., Bihannic, I., Soudant, P., Lambert, C., Huvet, A., 2017. Influence of environmental and anthropogenic factors on the composition, concentration and spatial distribution of microplastics: A case study of the Bay of Brest (Brittany, France). *Environmental Pollution* 225, 211-222.
- Gooch, J.W., 2011. *Encyclopedic Dictionary of Polymers*, 2<sup>nd</sup> Edition, Springer, 1015pp.
- Hansen, E., Nilsson, N.H., Lithner, D., Lassen, C., 2013. *Hazardous Substances in Plastic Materials*. Oslo: COWI and the Danish Technological Institute on behalf of The Norwegian Climate and Pollution Agency, 150 pp.
- Kaiser, D., Estelmann, A., Kowalski, N., Glockzin, M., Waniek, J.J., 2019. Sinking velocity of sub-millimeter microplastic. *Marine Pollution Bulletin* 139, 214-220.
- Koelmans, A.A., Kooi, N., Law, K.L., van Sebille, E., 2017. All is not lost: deriving a top-down mass budget of plastic at sea. *Environmental Research Letters* 12, 114028.
- Kooi, M., van Nes, E.H., Scheffer, M., Koelmans, A.A., 2017. Ups and downs in the ocean: Effects of biofouling on vertical transport of microplastics. *Environmental Science and Technology* 51, 7963-7971.
- Long, M., Moriceau, B., Gallinari, M., Lambert, C., Huvet, A., Raffray, J., Soudant, P., 2015. Interactions between microplastics and phytoplankton aggregates: Impact on their respective fates. *Marine Chemistry* 175, 39-46.
- Massos, A., Turner, A., 2017. Cadmium, lead and bromine in beached microplastics. *Environmental Pollution* 227, 139-145.

- Menzie, C.A., Southworth, B., Stephenson, G., Feisthauer, N., 2008. The importance of understanding the chemical form of a metal in the environment: The case of barium sulfate (barite). *Human and Ecological Risk Assessment* 14, 974-991.
- Mistri, M., Scoponi, M., Granata, T., Moruzzo, L., Massara, F., Munari, C., 2020. Types, occurrence and distribution of microplastics in sediments from the northern Tyrrhenian Sea. *Marine Pollution Bulletin* 153, 111016, DOI: 10.1016/j.marpolbul.2020.111016
- Mu, J., Qu, L., Jin, F., Zhang, S., Fang, C., Ma, X., Zhang, W., Huo, C., Cong, Y., Wang, J., 2019. Abundance and distribution of microplastics in the surface sediments from the northern Bering and Chukchi Seas. *Environmental Pollution* 245, 122-130.
- Nielsen E., Ladefoged, O., 2013. Barium, inorganic water-soluble compounds. Evaluation of health hazards and proposal of health based quality criteria for soil and drinking water. The Danish Environmental Protection Agency, Copenhagen. Available at: <https://www2.mst.dk/Udgiv/publications/2013/12/978-87-93026-71-1.pdf>
- Papazoglou, E.S., 2004. Flame retardants for plastics, in: C.A. Harper (ed.), *Handbook of Building Materials for Fire Protection*, McGraw-Hill, New York, pp 4.1-4.88.
- Pritchard, G., 1997. *Plastic Additives: An A-Z Reference*. Chapman and Hall, London, 633pp.
- Richard, H., Carpenter, E.J., Komada, T., Palmer, P.T., Rochman, C.M., 2019. Biofilm facilitates metal accumulation onto microplastics in estuarine waters. *Science of the Total Environment* 683, 600-608.
- Ropp, R.C. 2013. Group 16 (O, S, Se, Te) alkaline earth compounds. In: *Encyclopedia of the Alkaline Earth Compounds*. Elsevier, Amsterdam, 1187pp.
- Ryan, P.G., 2015. Does size and buoyancy affect the long-distance transport of floating debris? *Environmental Research Letters* 10, 084019, DOI: 10.1088/1748-9326/10/8/084019

- Schwarz, A.E., Ligthart, T.N., Boukris, E., van Harmelen, T., 2019. Sources, transport, and accumulation of different types of plastic litter in aquatic environments: A review study. *Marine Pollution Bulletin* 143, 92-100.
- Shaw, E.J., Turner, A., 2019. Recycled electronic plastic and marine litter. *Science of the Total Environment* 694, 133644.
- Turner, A., 2018. Concentrations and migratabilities of hazardous elements in second-hand children's plastic toys. *Environmental Science and Technology* 52, 3110-3116.
- Turner, A., Filella, M., 2017. Field-portable-XRF reveals the ubiquity of antimony in plastic consumer products. *Science of the Total Environment* 584-585, 982-989.
- Turner, A., Solman, K.R., 2016. Analysis of the elemental composition of marine litter by field-portable-XRF. *Talanta* 159, 262-271.
- Turner, A., Arnold, R., Williams, T., 2020. Weathering and persistence of plastic in the marine environment: Lessons from LEGO. *Environmental Pollution* 262, 114299.
- Vianello, A., Boldrin, A., Guerriero, P., Moschino, V., Rella, R., Sturaro, A., Da Ros, I., 2013. Microplastic particles in sediments of lagoon of Venice, Italy: First observations on occurrence, spatial patterns and identification. *Estuarine, Coastal and Shelf Science* 130, 54-61.
- Yin, L.Y., Chen, B.J., Xia, B., Shi, X.T., Qu, K.M., 2018. Polystyrene microplastics alter the behavior, energy reserve and nutritional composition of marine jacobever (*Sebastes schlegelii*). *Journal of Hazardous Materials* 360, 97-105.
- Zhang, H., 2017. Transport of microplastics in coastal seas. *Estuarine, Coastal and Shelf Science* 199, 74-86.



Table 1: Number of cases in which Ba was detected by XRF and summary statistics for Ba concentrations in consumer plastics and beached plastics. Also shown is the number of PVC samples containing detectable Ba.

	Consumer goods	Atlantic beaches	Urban beaches	Channel beach
no. analysed	342	95	55	43
no. Ba detected	140	6	11	1
% Ba detected	40.9	6.3	20.0	2.3
mean, mg kg <sup>-1</sup>	6890	2150	2540	910
min, mg kg <sup>-1</sup>	243	551	329	
max, mg kg <sup>-1</sup>	105,000	5690	10,700	
median, mg kg <sup>-1</sup>	1540	1620	2030	
Q1, mg kg <sup>-1</sup>	640	1130	1080	
Q3, mg kg <sup>-1</sup>	6510	2220	2700	
no. PVC	33	1	1	0
no. PVC Ba detected	26	0	1	0

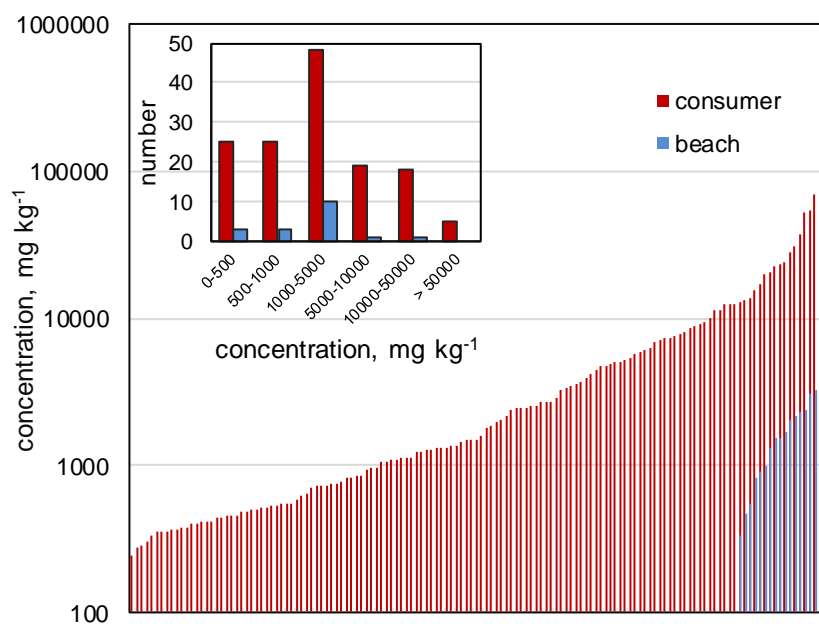


Figure 1: Barium detected in consumer and beached plastics, shown in ascending order of concentration. Inset is the frequency distribution of Ba concentrations in both categories.

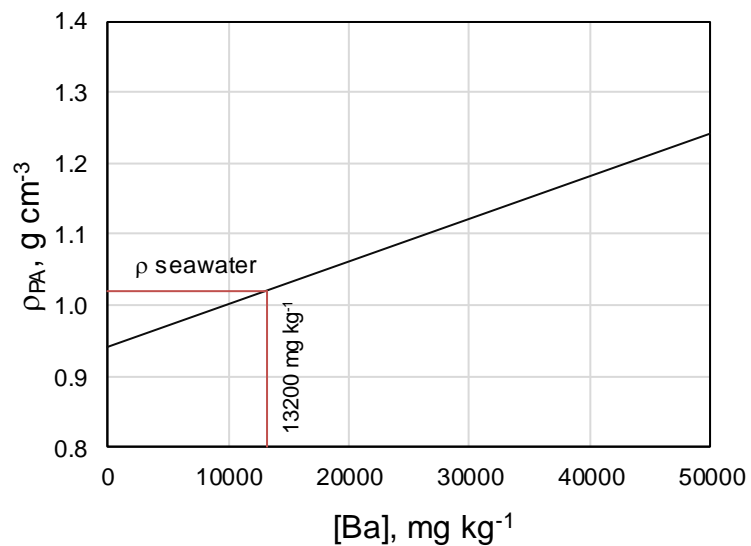


Figure 2: Increase in density of a polyolefin with increasing Ba content, calculated according to equation 2. Annotated is the density of coastal seawater and the (critical) added Ba content required to reach this value.